

The Chemistry and Transformations of Mercury and Arsenic in Anaerobic Sediments

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LONG TERM GOALS

Mercury and Arsenic are important pollutants released from a variety of sources (ships, buoy batteries, etc.) into harbors and coastal waters. Both these elements can have important ecological effects and bioaccumulation of mercury in fish is a concern for human health. We thus need to understand the factors that control the fate of arsenic and mercury in harbors and coastal waters. This project focuses on the transformations of arsenic and mercury in the anoxic sediments that are characteristic of such environs. More specifically, the long term goals of this project are to elucidate the chemical and biological mechanisms that control the precipitation and dissolution of arsenic and mercury in anaerobic coastal sediments and to quantify the consequences of these processes in determining the potential release of these toxic elements to the water column and their accumulation in marine organisms.

OBJECTIVES

The specific objectives of this project are to 1) document the microbial reduction of the relatively immobile arsenate to the more mobile arsenite in anaerobic sediments; 2) study the conditions for arsenate reduction and precipitation of arsenite as the arsenic trisulfide solid; 3) study the dissolution of mercuric sulfide under various conditions; 4) quantify the rates of oxidation and reduction of dissolved mercury; and 5) elucidate the chemical conditions that enhance the rate of microbial uptake and methylation of mercury in anaerobic sediments.

APPROACH

The arsenic part of the project is based chiefly on laboratory studies with bacteria collected in the field. By studying both isolated bacteria in pure cultures and natural consortia we seek to establish the importance of arsenate respiration (i.e. elucidate the conditions for its reduction to arsenite) and of arsenite precipitation in the environment and determine the factors that accelerate or inhibit these transformations.

Our mercury work (which has been put to a lower priority because of funding cuts) is also based chiefly on laboratory studies, both chemical and microbiological. The chemical studies have focused on the dissolution of cinnabar (solid mercuric sulfide the principal form of mercury in anaerobic sediments) to release ionic (Hg(II)) and elemental (Hg(0)) mercury, the reduction of

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Hg(II) to the volatile Hg(0), and the oxidation of Hg(0) to Hg(II). The microbial studies are designed to quantify the effect of medium chemistry on the rate of intracellular uptake of mercury by bacteria and on the rate of Hg(II) methylation.

WORK COMPLETED

As detailed in the publications listed below, the arsenic part of this project has led to a major advance in our understanding of the geochemistry of arsenic in anoxic sediments: we have established the existence and the importance of microbial respiration of arsenate (“dissimilatory arsenate reduction”) in anaerobic systems contaminated with arsenic. We have also demonstrated the microbial precipitation of arsenic trisulfide.

The mercury part of the project has demonstrated the importance of heretofore unknown redox and photoredox processes that affect the dissolution and volatilization of mercury. We have also disproved a seductive hypothesis according to which polysulfide complexation of ionic mercury could have enhanced mercury methylation rates in anoxic sediments.

RESULTS

Our results on arsenic have been published in a series of papers by Newman et al. and by Ahmann et al., including a succinct review. The highlights are:

- 1) The discovery of the arsenate respiration as a novel microbial metabolic pathway in the environment.
- 2) The demonstration that this process is common in bacteria isolated from As - contaminated sediments.
- 3) The establishment that biological precipitation of arsenic trisulfide may, in some cases, accompany arsenate respiration.
- 4) A partial characterization of the respiratory enzyme responsible for arsenate reduction.

This work is now being continued and expanded by a number of research groups around the country. Soon molecular probes should be available to conveniently assess the occurrence of arsenate respiration in the field.

The results obtained for mercury have also been published in a series of papers (by Mason et al. and Amyot et al.) and are still being published. A recent review by Morel et al. summarizes those results:

- 1) Photochemical formation of gaseous elemental mercury.
- 2) Oxidation by oxygen of elemental mercury (in the presence of chloride).

3) Photochemical dissolution of mercuric sulfide (cinnabar).

In addition we have also tested the hypothesis (which we had formulated but which others had picked up) that the formation of polysulfide complexes of mercury (S_nHg) might greatly enhance the rate of mercury methylation by sulfate reducing bacteria. We have now convincingly disproved this hypothesis. Polysulfide appears to play only an insignificant and indirect role in mercury methylation.

IMPACT

These results have modified radically our understanding of the processes that control the fate of arsenic and mercury in coastal waters. First it appears that arsenate respiration is likely widespread among bacterial phyla and common in contaminated anoxic environs. Further, the microbial precipitation of arsenic trisulfide, puts into question the general assumption that reduction of As(V) to As(III) makes As more mobile in the environment. On the contrary, As_2S_3 precipitation may provide a permanent sink for As in anaerobic sediments.

For mercury, our finding that $Hg(0)$ can be rapidly oxidized in seawater implies that in many coastal waters where this process should effectively decrease the net rate of $Hg(0)$ volatilization, we have likely overestimated the rate of mercury release into the atmosphere.

TRANSITIONS

Our results on $Hg(0)$ oxidation are of great importance regarding the fate of elemental mercury released from discarded Aids to Navigation.

RELATED PROJECTS

This ONR project benefits from two ongoing projects (funded by EPA and NSF) dealing with the microbiology and chemistry of arsenic and mercury.

REFERENCES

Publications Relating to Arsenic:

Newman, D.K., R.S. Oremland, P.R. Dowdle, F.M.M. Morel, and J.F. Stolz. Purification and characterization of the dissimilatory arsenate reductase from *Sulfurospirillum barnesii* strain SES-3. *Proc. Nat. Acad. Sci.*, (in revision).

Newman, D.K., D. Ahmann, and F.M.M. Morel. A brief review of dissimilatory arsenate reduction. *Geomicrobio. Jour.*, 15: 1-14 (1998).

Ahmann, D., L.R. Krumholz, H.H. Hemond, D.R. Lovley, and F.M.M. Morel. Microbial mobilization of arsenic from sediments of the Aberjona Watershed. *Env. Sci. Tech.*, 31: 2923-2930 (1997).

Newman, D.K., E.K. Kennedy, J.D. Coates, D. Ahmann, D.J. Ellis, D.R. Lovley, and F.M.M. Morel. Dissimilatory As(V) and S(VI) reduction in *Desulfotomaculum auripigmentum*, sp. nov. *Archives Microbiol.*, 168: 380-388 (1997).

Newman, D.K., T.J. Beveridge and F.M.M. Morel. Precipitation of As_2S_3 by a novel As(V)-reducing bacterium, strain OREX-4. *Appl. Env. Microbiol.*, 63: 2022-2028 (1997).

Ahmann, D., A.L. Roberts, L.R. Krumholz, and F.M.M. Morel. Microbe grows by reducing arsenic. *Nature*, 371: 750 (1994).

Publications Relating to Mercury:

Morel, F.M.M., A.M.L. Kraepiel, and M. Amyot. The chemical cycle and bioaccumulation of mercury. *Annual Review Ecology and Systematics*, Vol. 29, (in press).

Amyot, M., G.A. Gill, and F.M.M. Morel. Production and loss of dissolved gaseous mercury in coastal seawater. *Env. Sci. Tech.*, 31: 3606-3611 (1997).

Mason, R.P., J.R. Reinfelder and F.M.M. Morel. The uptake, toxicity, and trophic transfer of mercury in a coastal diatom. *Env. Sci. Tech.*, 30: 1835-1845 (1996).

Mason, R.P., F.M.M. Morel and H.F. Hemond. The role of microorganisms in elemental mercury formation in natural waters. *Water Air Soil Pollut.*, 80: 775-787 (1995).

Mason, R.P., J.R. Reinfelder, and F.M.M. Morel. Bioaccumulation of mercury and methylmercury. *Water Air Soil Pollut.*, 80: 915-921 (1995).